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(54) Electrochemical sensor construction

(57) A compact electrochemical measuring electrode device (1) constructed in thick film technique on a plane circular substrate (13) of a ceramic material such as alumina, the electrodes (14, 15) of the electrode device being arranged on one side of the substrate, and the electrical connections (20, 26, 27) being arranged on the other side of the substrate. In the substrate, a through-going passage is provided for establishing electrical junction between an electrode (14) and an associated electrical connection, and a metallic conductor is introduced into the passage, preferably in the form of a rivet or a solidified metal paste. A terminal is applied in thick film technique on one side of the electrode device, and an elec-

trode layer (14) is provided in thick film technique on the other side, both in direct electrically conductive connection with the conductor. Several layers of electrode material are applied, the area of the layers being reduced to provide a stepped configuration. In a polarographic electrode device, the cathode is platinum wire embedded in glass tube and secured and sealed in the through-going passage by means of glass paste heated to above its normal application temperature.

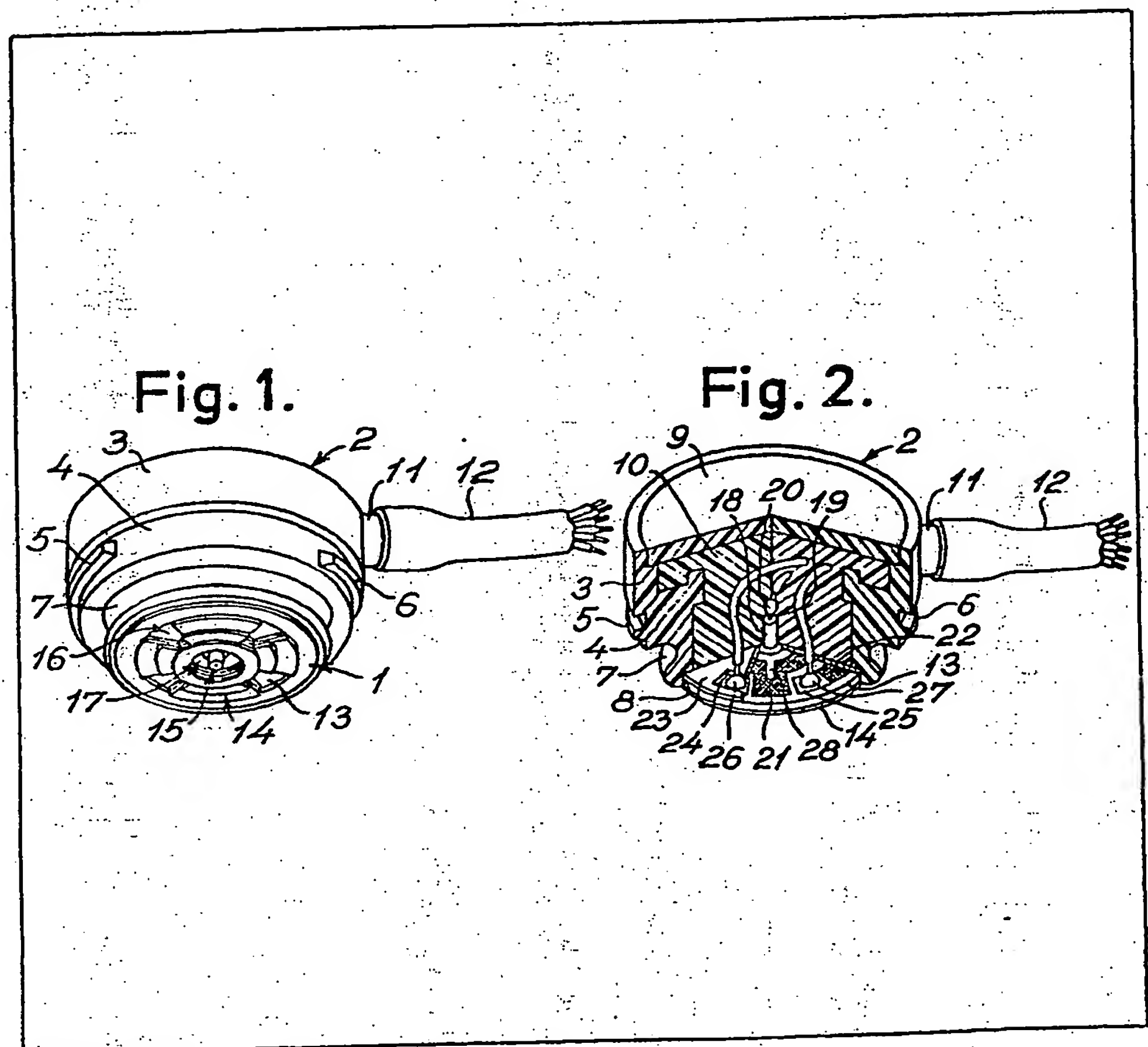


Fig. 1.

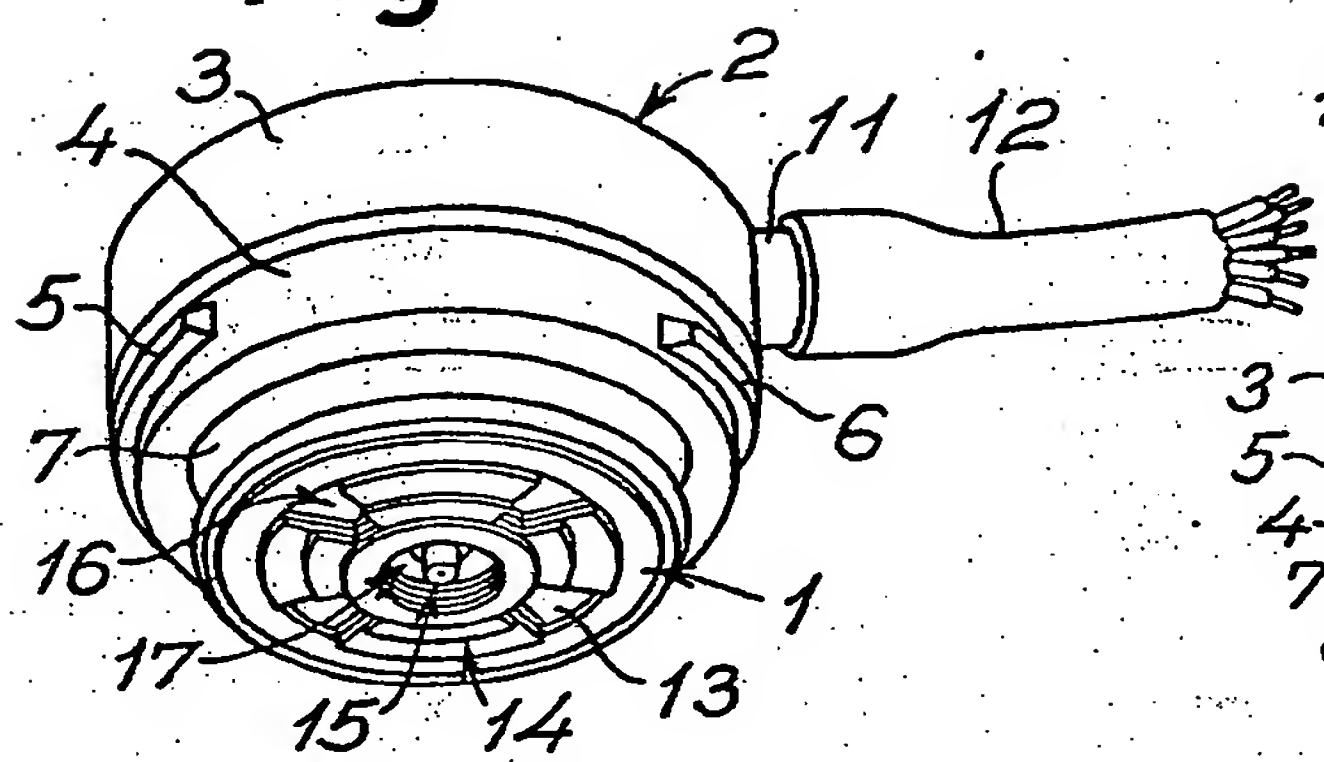


Fig. 2.

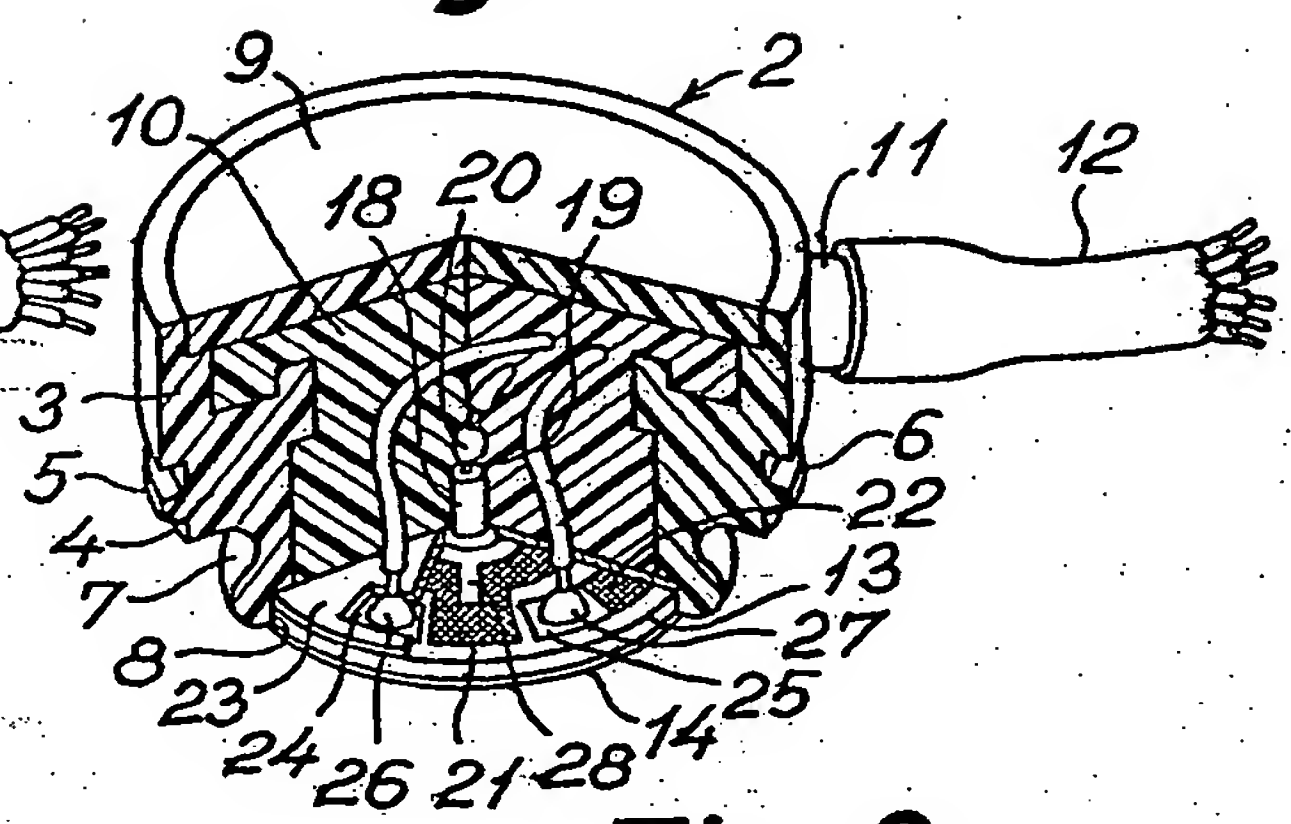


Fig. 3a.

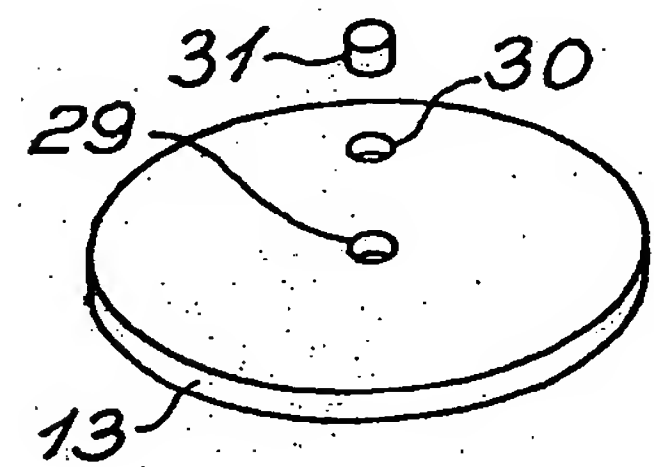


Fig. 5.

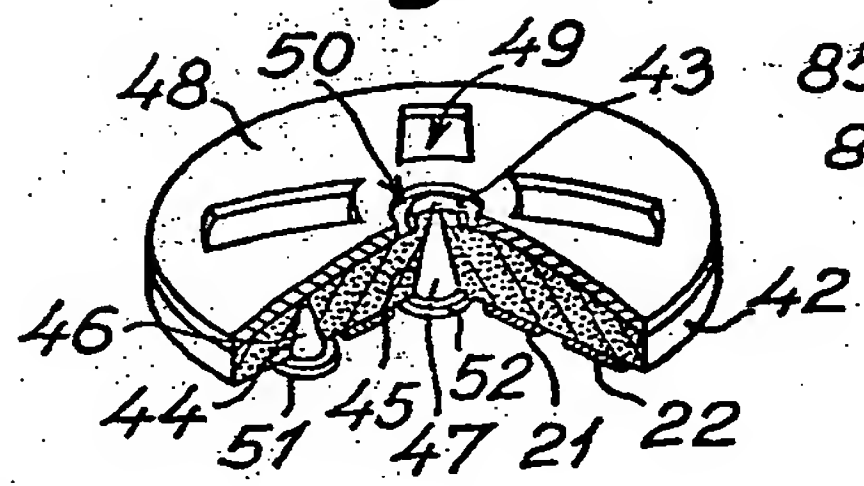


Fig. 8.

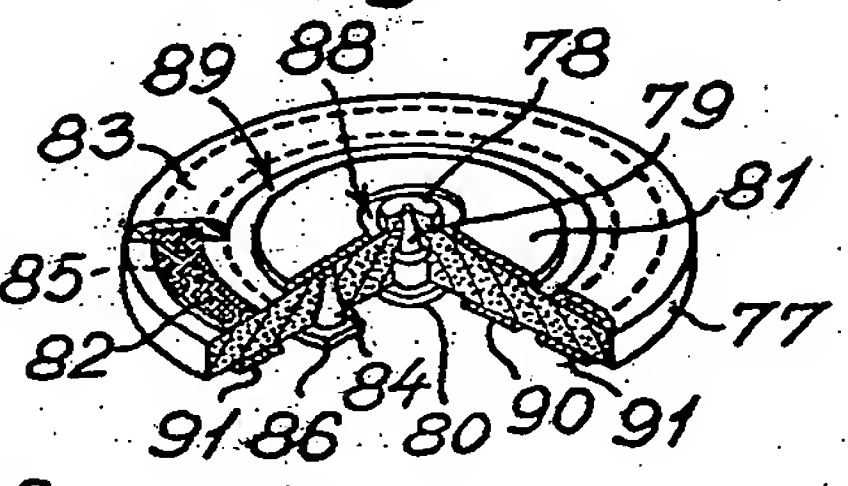


Fig. 3b.

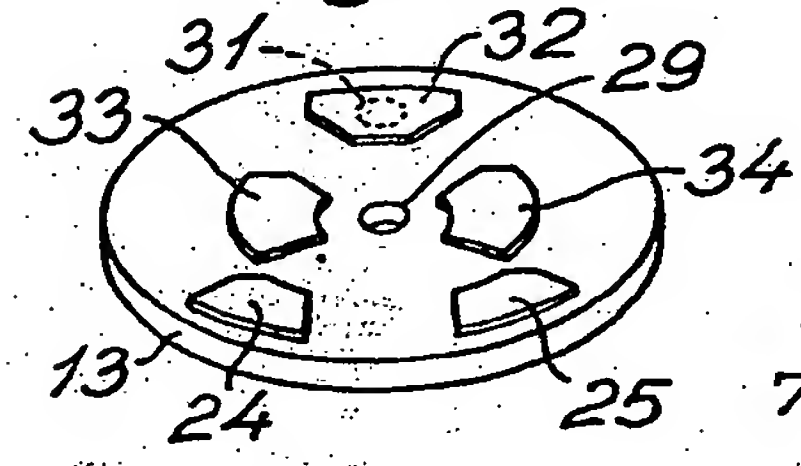


Fig. 6.

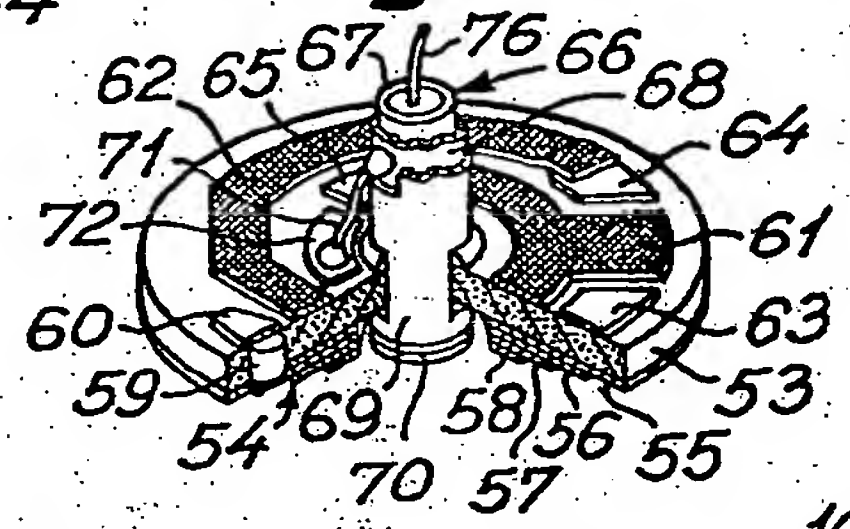


Fig. 9.

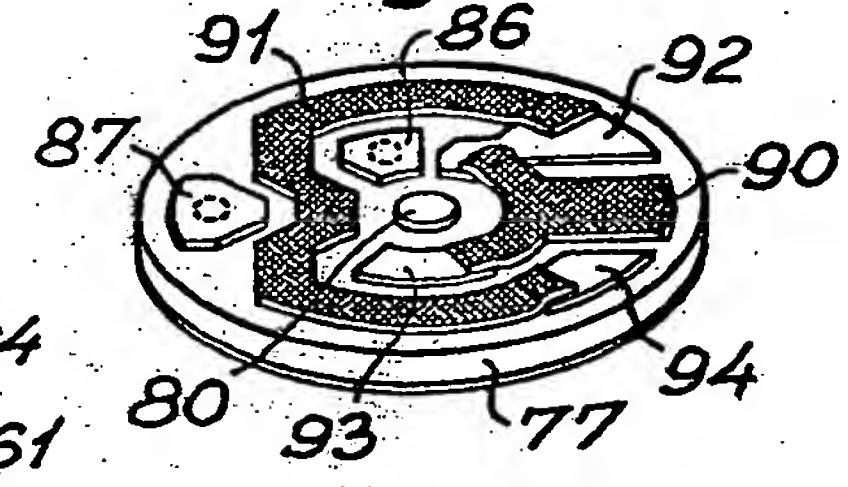


Fig. 3c.

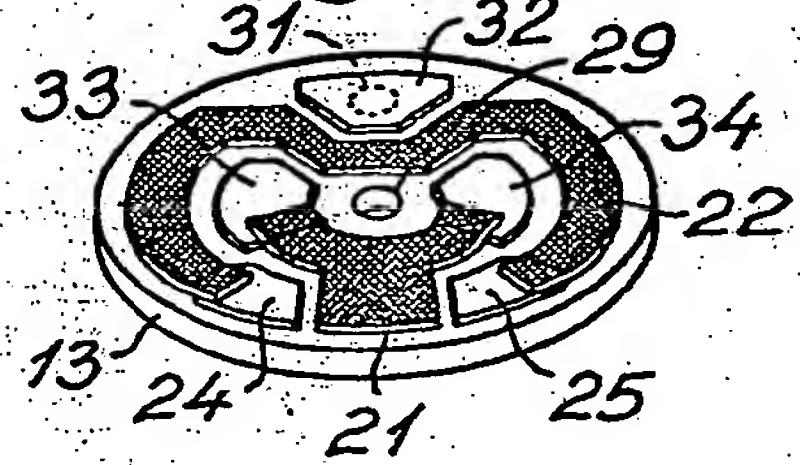


Fig. 10.

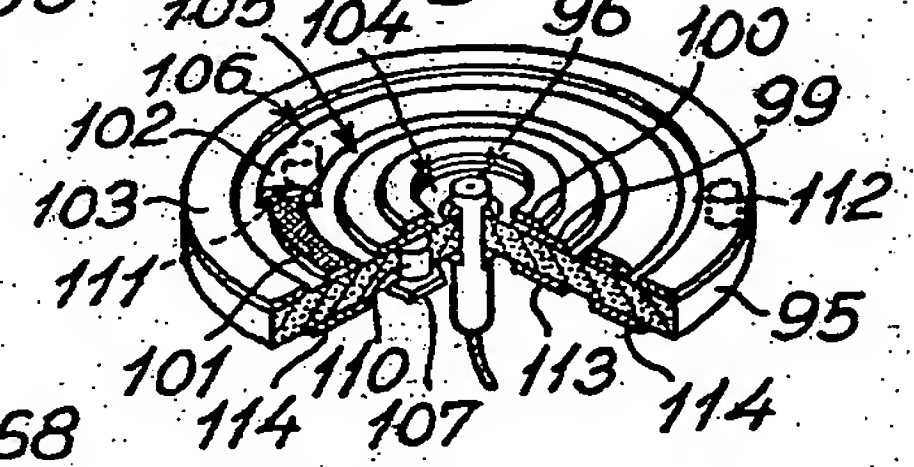


Fig. 4.

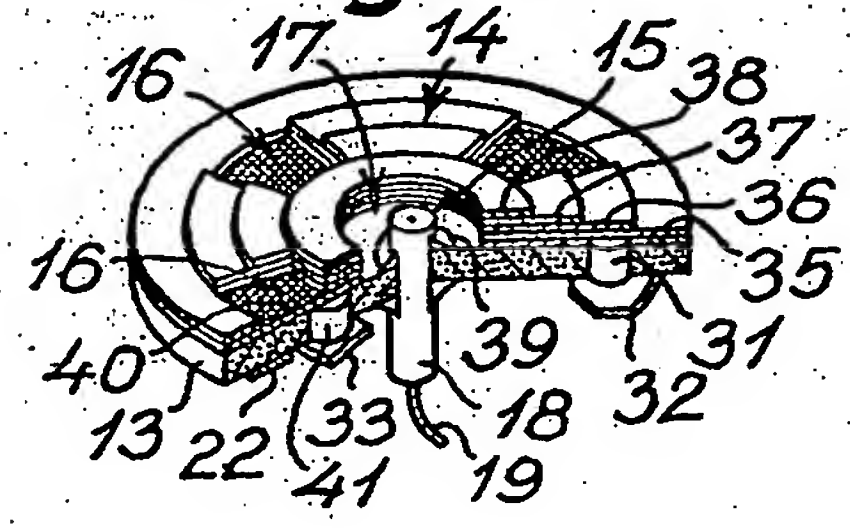


Fig. 7.

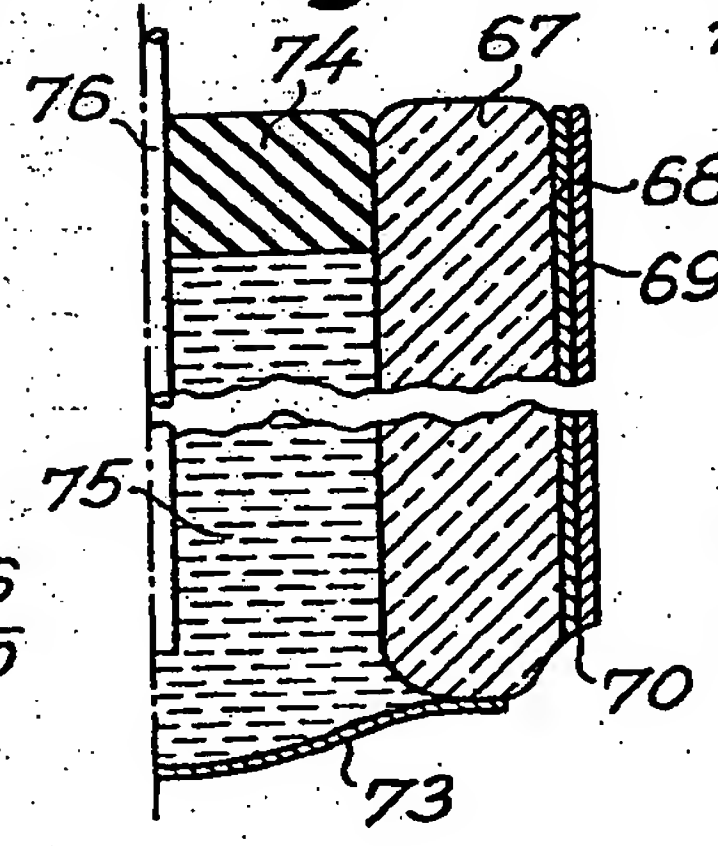


Fig. 11.

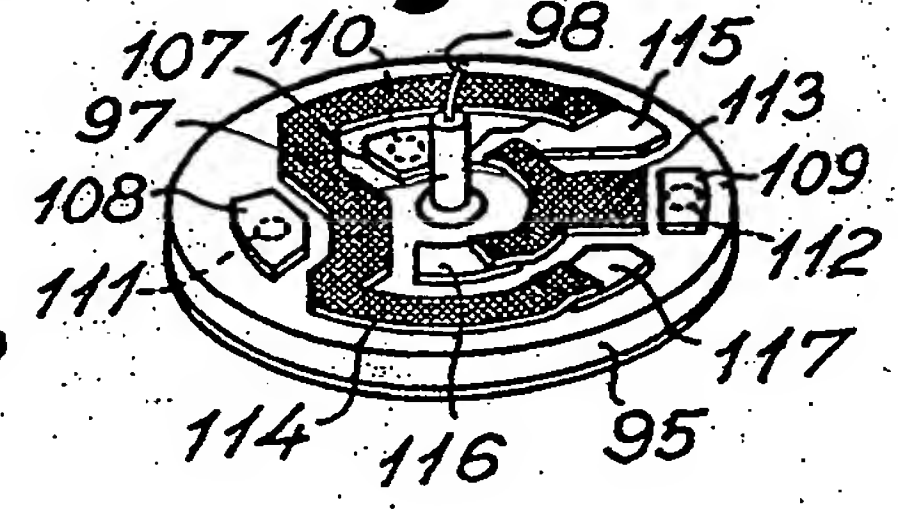


Fig. 12.

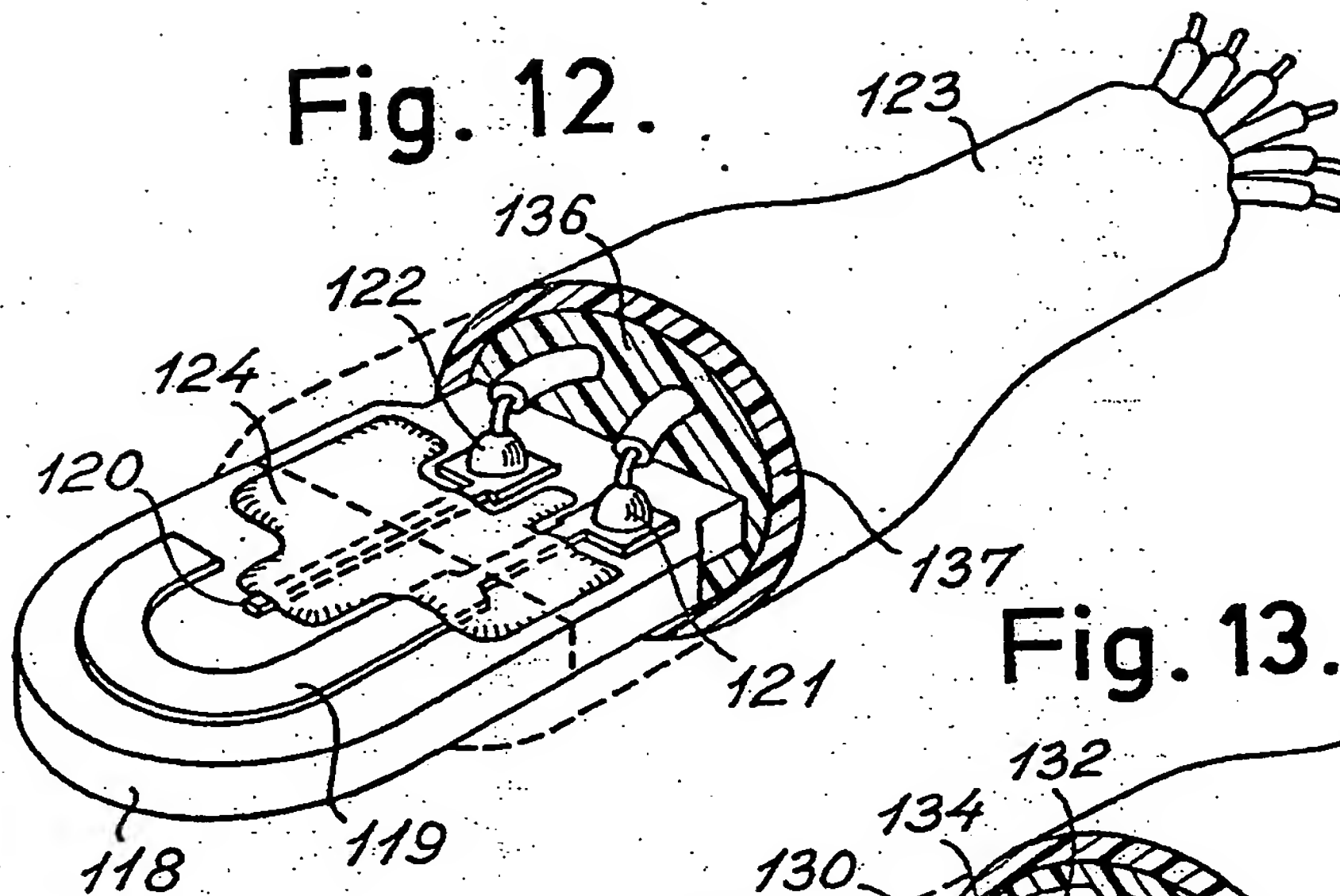


Fig. 13.

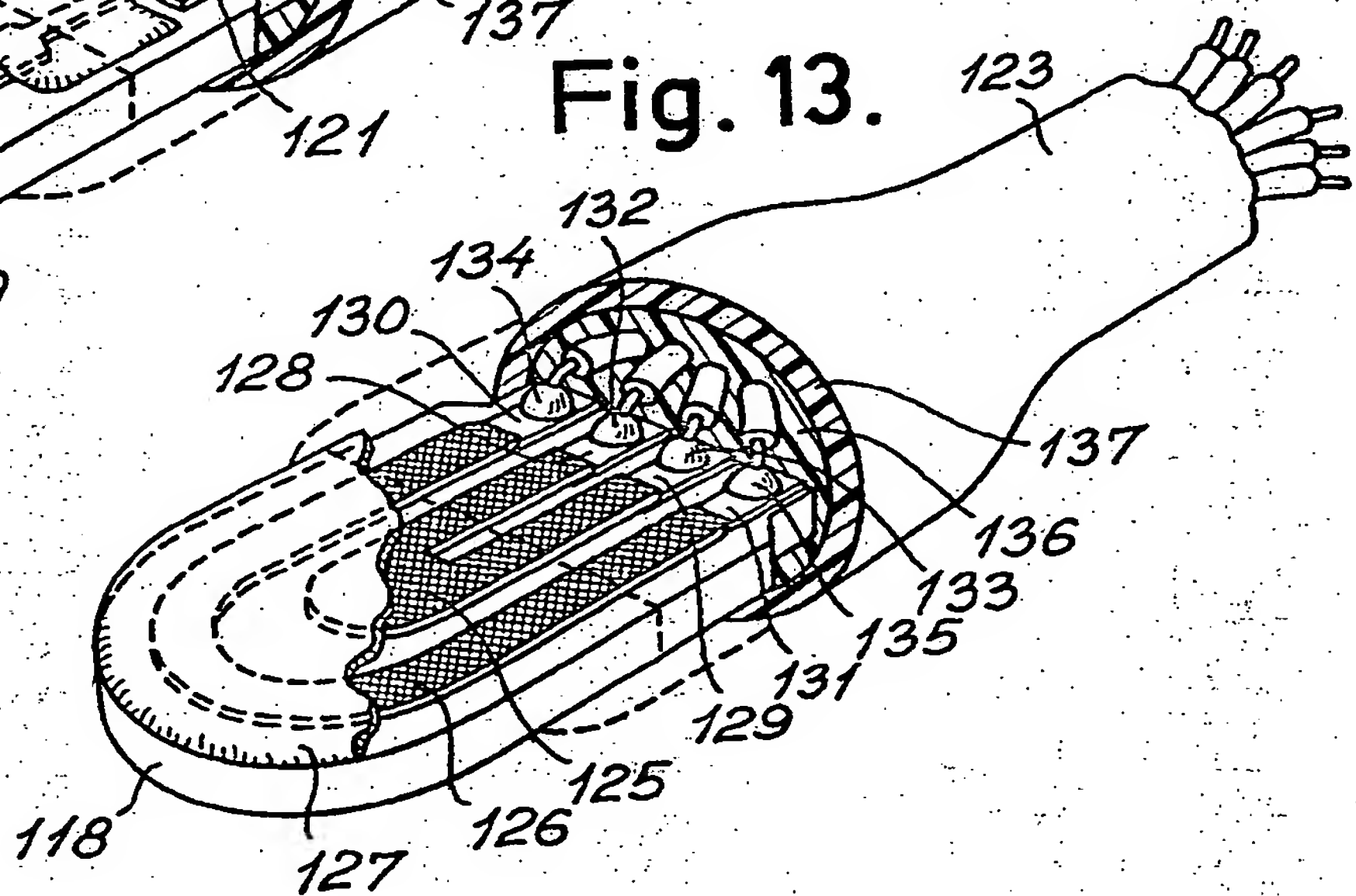


Fig. 14.

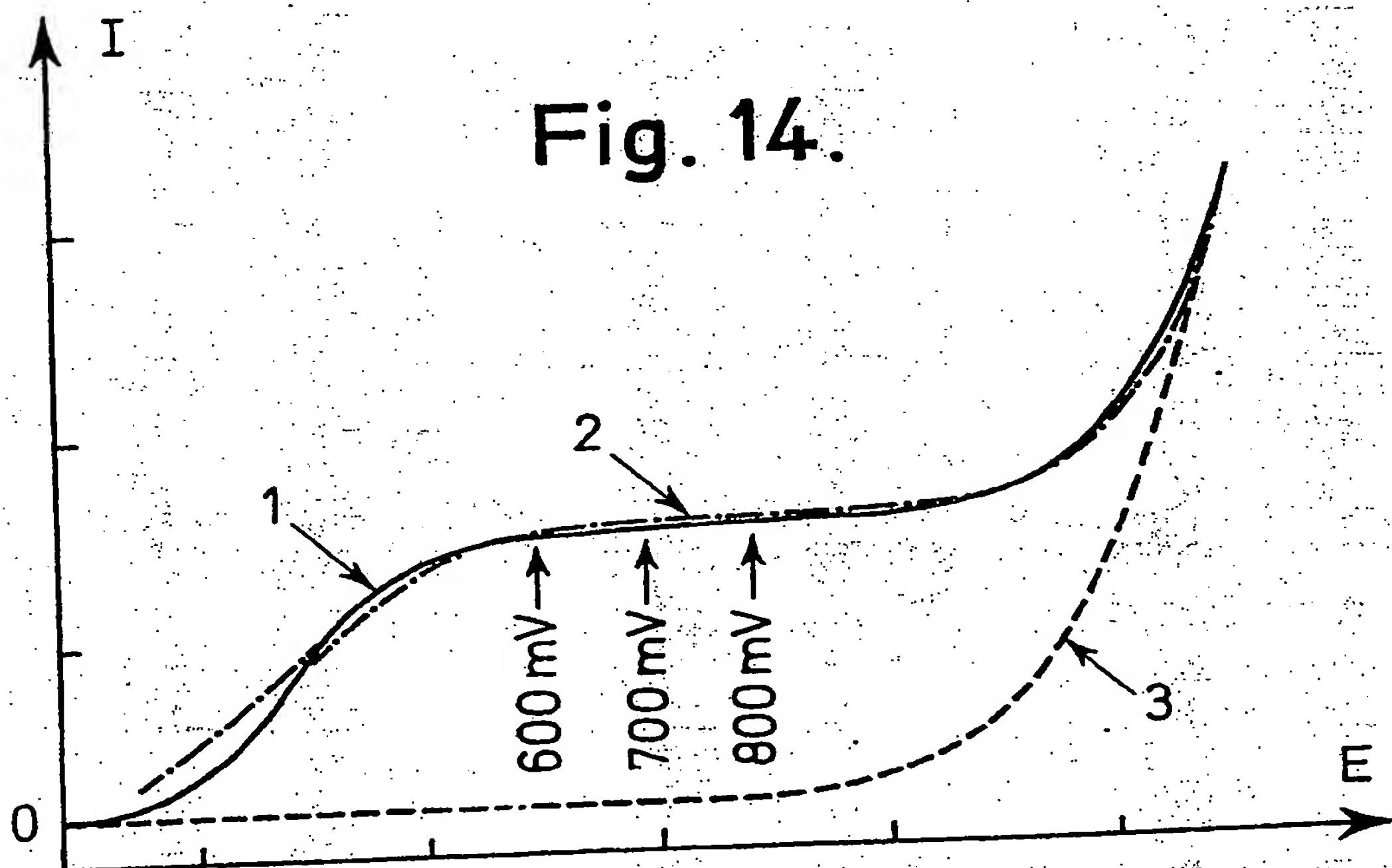


Fig. 15.

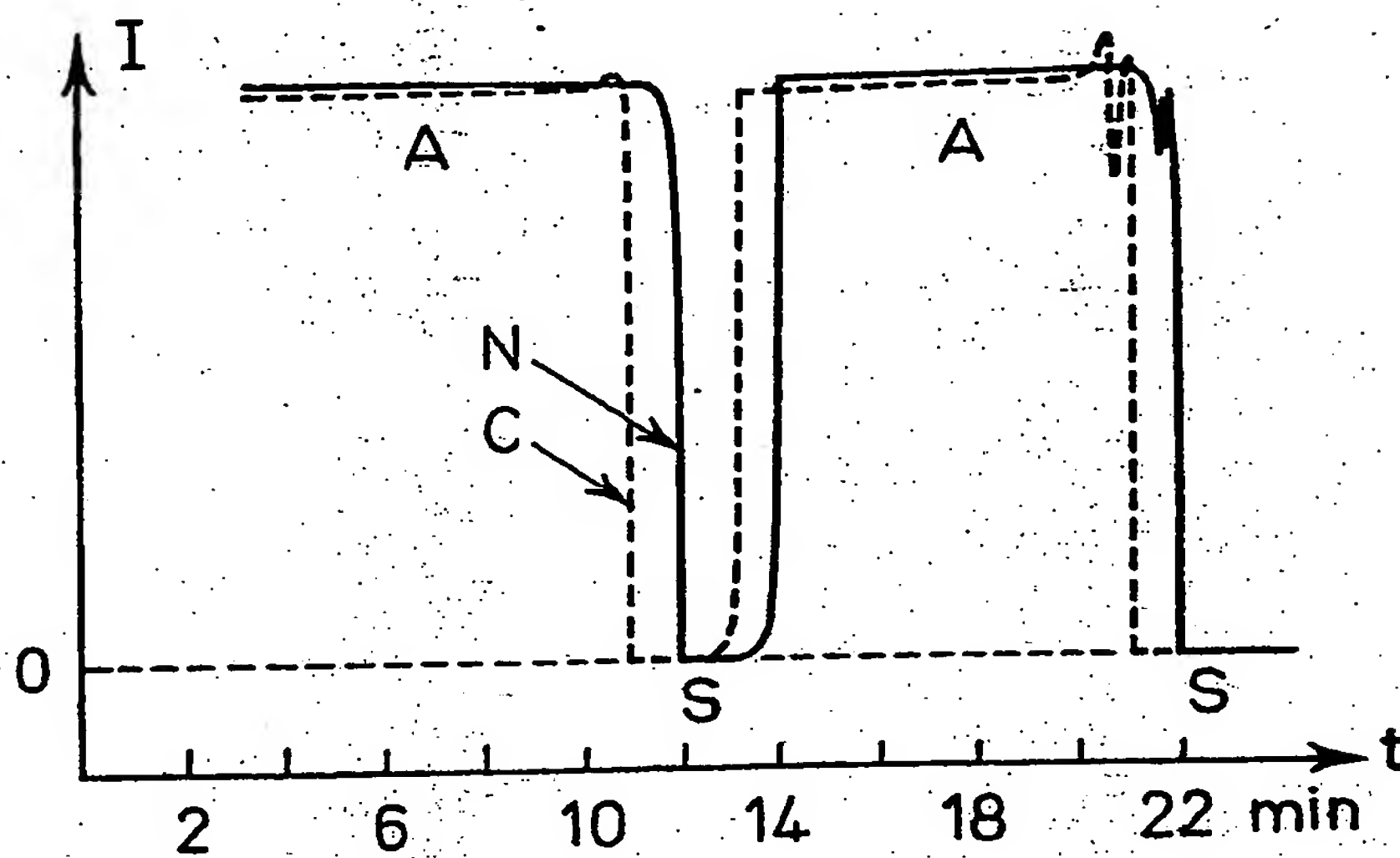


Fig. 16.

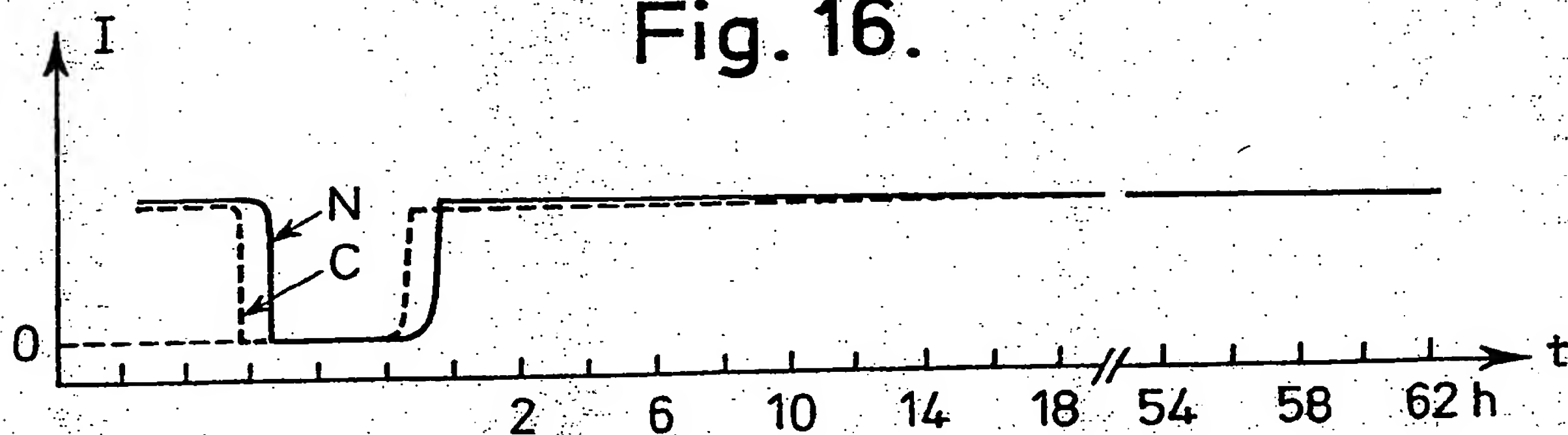
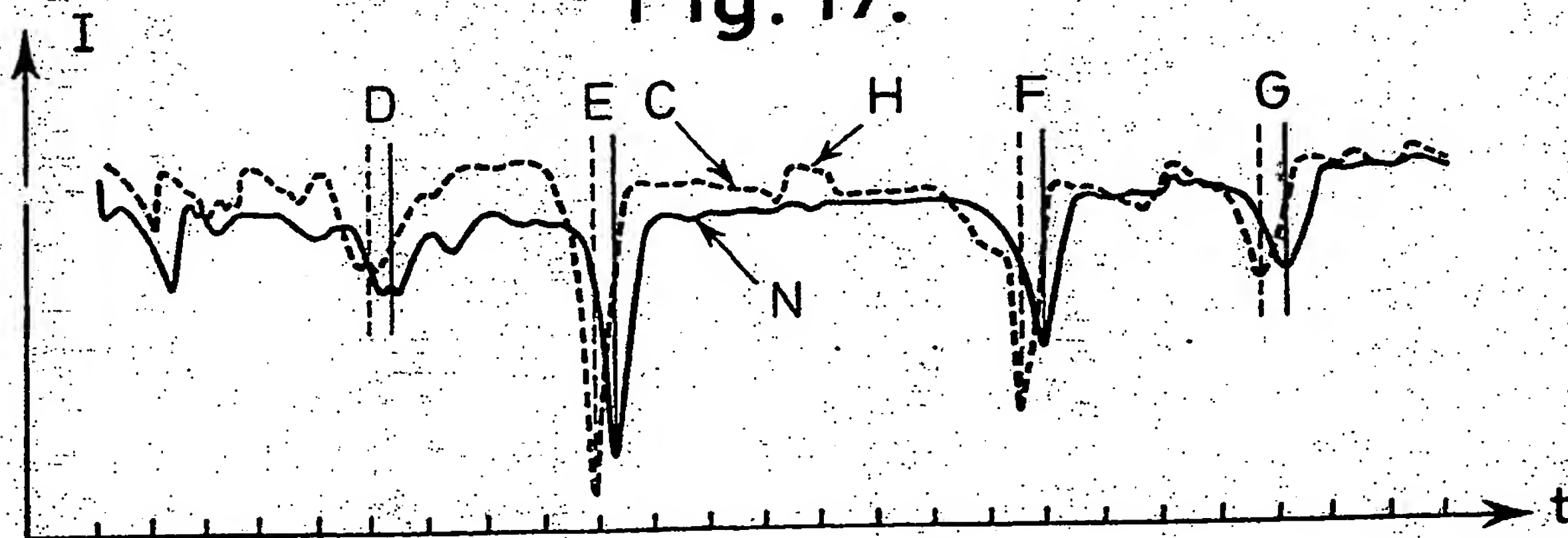


Fig. 17.



SPECIFICATION

Electrochemical measuring electrode device and method for its preparation

5 The present invention relates to an electrochemical measuring electrode device and a method for its preparation.

10 Electrochemical measuring electrode devices for the determination of, e.g., pH or the partial pressure of a gas in a liquid or a gas mixture, have been produced and suggested in several different embodiments. Common to all known measuring electrode devices which
15 are able to produce reliable measuring results during long periods of time is the fact that they are relatively expensive to produce due to their relatively complicated mechanical construction and the highly critical requirements
20 to their individual components.

Several attempts have been made to prepare measuring electrode devices of a more simple construction which could be produced at a lower cost and/or implemented in smaller
25 dimensions. However, none of these attempts have hitherto resulted in measuring electrode devices which compare favourably with the above-mentioned, highly reliable measuring electrode devices with respect to the reliability
30 of their measuring results, their mechanical sturdiness, and their ability to maintain their characteristics during long periods of time.

The present invention provides electrochemical measuring electrode devices which are
35 at least as good as the best types of known electrochemical measuring electrode devices with respect to the quality of their measuring results, their mechanical sturdiness, and their ability to maintain their characteristics during
40 long periods of time, but which, by utilization of unconventional technology, can be produced in a far more simple and rational way than known measuring electrode devices, thus permitting more rational mass production.

45 Furthermore, the invention provides completely new possibilities for a compact construction of the measuring electrode devices which is superior to known measuring electrode devices with respect to application technique and reliability. The measuring electrode
50 devices according to the present invention also provide a substantial saving of materials, including a substantial saving of expensive materials, compared to similar known measuring electrode devices.
55

In one of its aspects, the electrochemical measuring electrode device according to the invention comprises an electrically insulating
60 substrate and at least one electrode prepared in thick film technique and arranged on one side of the substrate (and normally at least one further electrode arranged on the same side of the substrate for establishing a measuring cell in cooperation with the thick film
65 electrode); the device comprising electrically

conductive means adapted for establishment of electrical connection to the electrode and provided on a side of the substrate which is different from the side on which the thick film
70 electrode is arranged, and the electrical junction between the electrode prepared in thick film technique and said electrically conductive means being constituted by an electrical conductor arranged in a through-going passage in
75 the substrate.

Thick film technique is a known technique comprising: applying materials in the form of paste containing an active component, a temporary binder and a permanent binder on a
80 temperature resistant substrate, and subsequently removing the temporary binder and hardening the permanent binder. The paste is applied in a silk screen printing process using a silk screen printing mask. This mask may be
85 produced in different ways, including manual or automatic production. A feasible manual production process may include production of a cutting film from a specified graphical figure representing the desired contours of the paste
90 after application, photographic conversion of said cutting film into correct scale on a so-called lith-film, application of a light sensitive emulsion on a silk screen printing mesh, exposing the silk screen printing mesh to UV-
95 light through the lith-film, and washing the silk screen printing mesh.

The silk screen printing process is normally carried out automatically. A substrate on which the paste is to be applied is fixed in a
100 specially constructed holder by means of vacuum fixing, and the silk screen printing mesh described above is centered relative to the substrate and is fixed relative to said holder. The holder, which fits into the silk screen
105 printing apparatus, is introduced therein, and the paste is applied onto the substrate by squeegeeing (application by means of a squeegee or spatula) through the silk screen printing mesh.

110 Typically, the paste comprises the following four main components: (1) the active material comprising metal or metal oxide, (2) a glass frit serving as permanent binder, (3) organic constituents, partly a volatile constituent (for
115 example butyl "cellosolve" acetate) and partly a non-volatile component (for example ethoxyl), which together constitute the temporary binder, and (4) a viscosity controlling agent, e.g., a small amount of pine oil. After
120 the printing, the procedure is typically as follows: the substrate with the printed wet paste is placed in a furnace and is pre-dried so that the volatile component of the temporary binder system is evaporated, e.g., at a
125 temperature of 130°C for 15 minutes. Subsequently, the dried, printed substrate is transferred to a conveyor furnace and is subjected to a high temperature treatment. A normal temperature profile comprises a heating period of approximately 10-15 minutes, from
130

about 20°C to about 850°C, a temperature gradient of 80–100°C per minute being aimed at, during which period the non-volatile part of the temporary binder system is burned away, and thereafter a holding time of about 10 minutes at 850°C where the permanent binder bonds to the substrate and bonds the active material in such a manner that the active material undergoes a kind of sintering or vitrification and generates an electrically conductive layer. Thereafter, a controlled cooling is performed in the course of 10–15 minutes.

According to the present invention, the electrical junction between the electrode prepared in thick film technique and the electrically conductive means (typically electrical cores, electrical terminals fields or pins for soldered joints with electrical cores, or terminals of printed circuits) for establishing electrically conductive connection between the electrode and co-operating external equipment is constituted by an electrical conductor arranged in a through-going passage in the substrate. The through-going electrical junction between the thick film electrode and its electrical connections is established in a very advantageous manner using novel techniques which are aspects of the present invention and which are disclosed below and is a critical condition for the utilization of the advantages of the thick film technique in connection with electrochemical measuring electrode devices, as it permits the necessary absolutely effective sealing of the connection side of the substrate relative to the active measuring side of the electrode device.

Typically, the substrate has a plane or plane-convex shape, and the electrically conductive means are provided on the plane side of the substrate. In this manner, a universally applicable electrode unit is provided which, in particular when having a substantially circular shape, is optimally adapted to being built into holders or housings of any kind and for any purpose for which electrochemical measuring electrode devices have been used. The fact that the electrical junction is placed in a through-going passage also permits mechanical treatment of the substrate periphery, such as grinding or polishing for exact adaption to any holder or housing.

The electrically conductive means are suitably constituted by connection or terminal fields adapted for establishing soldering joints with electrical cores of a cable for connection to external associated equipment. Preferably, the terminal fields are also prepared in thick film technique.

The establishment of the electrical conductor in a through-going passage in the substrate may, according to the invention, be obtained by means of a metal rivet (typically a silver rivet) press-fitted into the passage, by means of a body of metal paste of the above-

mentioned kind adapted for use in the thick film technique (e.g., silver, gold, or platinum paste) or metal (e.g., platinum) solidified in the passage, or by embedding the conductor in a glass tube and securing and sealing the glass tube in the passage by means of superheated glass paste. All of these techniques are described in greater detail in the following. It is of decisive importance to the proper function of the electrode device of the invention that the electrical junctions established through the substrate do not to any extent allow water to penetrate. In this regard, the above-mentioned techniques according to the invention for establishing the junction have been found to result in optimum sealing and tightness.

The optimum utilization of the thick film technique provided by the present invention makes it possible to combine several electrode measuring principles and/or one or more electrode measuring principles and further measuring means and/or controlling means, typically, e.g., temperature measuring and heating means for achieving thermostating, still will obtainment of a hitherto unattainable compact construction.

Thus, e.g., electrochemical measuring electrode devices, especially for measurement of gas partial pressures, particularly for transcutaneous measurement of the partial pressure of oxygen and/or carbon dioxide in blood, should, on the one hand, be so small and compact that they can be practically arranged and maintained on the skin, but must, on the other hand, comprise the necessary electrodes and means for thermostating, i.e. temperature measuring means and heating means. According to the present invention, an extremely compact construction of such electrode devices is obtained when these circuits are also constructed in thick film technique. The thermostating circuit may, e.g., comprise a temperature-dependent resistor such as an NTC-resistor applied in thick film technique and serving both temperature measuring and heating purposes, or it may comprise a combination of an NTC-resistor and a heating resistor, both applied in thick film technique, preferably on the opposite side of the substrate relative to the thick film electrode. In comparison to thermostating circuits constructed in discrete components, thermostating circuits applied in thick film technique offer the advantage that no insulating layer is located between on the one hand the active temperature sensing component and the active heating component and on the other hand the body to be thermostated. A further advantage associated with the application of thick film technique for the thermostating circuits is that the necessary thermostating accuracy may be achieved by simple trimming of the thermostating circuits applied in thick film technique, e.g., by means of a laser beam or by sand

5 blasting instead of using expensive components having low tolerances. The compactness obtained by use of the principles according to the present invention further permits a more effective heat insulation relative to ambience than may be achieved using electrode devices constructed from discrete components so that the power consumption of the electrode device may be reduced, which is of great importance when measuring in oxygen enriched environments.

10 On the other hand, the well-known compatibility between thick film technique and discrete components makes it possible to combine the electrode device of the invention with discrete components for, e.g., the thermostating circuit whenever this is desired.

15 In the known art, thick film technique has been suggested for the preparation of an ion-sensitive half cell, cf. US Patent Specification No. 4,133,735. However, this half cell, including the electrical connections to the electrode, is constructed exclusively on one side of a substrate. From an abstract from a lecture made at the IEEE Biomedical Conference at Denver Hilton Hotel, October, 1979, a transcutaneous oxygen system is known comprising a plane circular substrate having a central hole in which a cathode, a 75 μm gold wire, is fixed by potting in polyester resin, and comprising a silver/silver chloride anode applied on the front side of the substrate in thick film technique (single layer) and a heat resistor and a thermistor applied to the rear side of the substrate in thick film technique. The abstract does not disclose how the electrical conductors to the anode are established and, in particular, does not disclose or indicate the critical feature of the present invention, that is, an electrical junction to the thick film electrode constituted by an electrical conductor arranged in a through-going passage in the substrate.

20 One special aspect of the present invention relates to measuring electrode devices including a silver electrode prepared in thick film technique and typically used either as a reference electrode for a pH-sensitive electrode or as an anode in a polarographic oxygen measuring electrode.

25 When the reference electrode for pH-sensitive electrode is constructed as a silver electrode in thick film technique, a substantial material saving relative to conventional silver reference electrodes is achieved. In polarographic measuring electrodes comprising a silver anode, the silver anode is consumed in the electrode process. However, according to the invention, it has been found that in spite of that, stable, long term reliable, high quality electrode devices may be obtained, provided that the silver electrode has an average thickness of more than 30 μm , preferably an average thickness in the interval 50–70 μm , typically an average thickness of about 65

30 μm . Silver electrodes of such thickness may be provided either by application of a layer of the silver paste by use of a mesh which provides a sufficiently thick layer, or by application of several layers of the silver paste, one on top of the other, for example in accordance with a stepped construction, the importance of which will be described below.

35 In the polarographic measuring electrode devices for the measurement of oxygen partial pressure, the cathode may suitably be constructed as a microcathode of a noble metal wire of a diameter of, e.g., 15–40 μm such as a platinum wire, which extends through the substrate in an electrically insulating encasing. According to an aspect of the invention, such a cathode may effectively be established by embedding a noble metal wire, e.g., a platinum wire, in a glass tube which is cast in a hole in the substrate by means of a glass paste. It has been found that glass paste of the type used in thick film technique for covering and protecting purposes shows uniquely advantageous properties as filling, stopping and sealing material for securing and tightening such a glass tube-embedded metal wire in a thick film substrate when the glass paste is used in an unconventional manner: The glass paste is introduced into the gap between the glass tube and the wall of the passage in the substrate through which the tube extends by heating the glass paste to such a temperature (in excess of the normal heating temperature of the glass paste) that it becomes low-viscous and fills and seals the gap, and thereafter allowing the glass paste to solidify by cooling. By this operation, the glass paste apparently combines with on the one hand the substrate and on the other hand the glass tube so as to form a microtight seal. Typically, the glass paste is heated to about 650–700°C which is about 200°C higher than the temperature to which such paste conventionally is heated.

40 The through-going passage or passages in the substrate may be generated by any appropriate technique, e.g. by drilling, or by introducing the passages during the fabrication of the substrates. However, a particularly suitable technique for generating exactly defined through-going passages in the substrate is by using a laser. The utilization of laser technique, furthermore, makes it possible to generate microfine passages in the substrate, such as passages of a diameter of as little as, e.g., 1–100 μm , such as 10–100 μm , e.g. 25–100 μm .

45 A specially interesting method according to the invention for establishing a noble metal cathode is to solidify a noble metal paste, e.g., gold or platinum paste, or molten noble metal such as platinum, in a suitably shaped passage in the substrate, e.g., a laser-established passage having a diameter of 25–100 μm . Such a passage will normally have a shape which is substantially conical, the diam-

eter being larger on the side of the substrate from which the laser beam was introduced. The orifice of the passage having the smaller diameter defines the active measuring surface of the cathode body solidified in the passage.

A suitable method for introducing molten metal or metal paste in the through-going passage is to suction or press the melt or paste into the passage by applying a pressure difference between opposite sides of the substrate. When molten metal is introduced, the solidification is obtained by allowing the metal to cool. When a metal paste is introduced, the solidification is obtained by heating the paste to its prescribed temperature so that it is bonded to the wall of the passage in the substrate.

It will be understood that in the same manner as the cathode in a polarographic electrode device according to the invention may be provided by one of the methods described above, also other electrodes of an electrode device according to the invention may be provided, that is, embedded in a glass tube and secured by means of superheated glass paste, or made from solidified molten metal or solidified metal paste. It has already been mentioned above that particular features of the present invention are the establishment of the electrical junction between a thick film electrode and its terminal field or other connecting means by solidifying metal paste in a through-going passage in the substrate and the press-fitting of a metal rivet. It will be understood that the method of the invention comprising securing and sealing a glass tube-embedded metal wire or metal conductor body by means of superheated glass paste may also be used for establishing the electrical junction between a thick film electrode and its terminal field or other connection. These three methods of establishing electrically conductive bodies in sealed through-going passages in the substrate may be combined in any manner suitable for the particular electrode device to be produced.

When the electrode device according to the invention is adapted for the measurement of the partial pressure of a gas in blood, either *in vitro* or *in vivo*, in particular in accordance with the so-called transcutaneous or non-invasive technique, the electrode device comprises, in a manner known *per se*, a membrane permeable to the gas in question and an electrolyte solution located between the membrane and the active measuring surface of the electrode or electrodes. Also in this case, the most suitable shape of the substrate of the electrode device is the substantially circular shape which facilitates proper stretching of the membrane over the surface of the electrode and permits an easy and effective mounting of the substrate in an electrode housing.

In a particularly elegant construction of this

type of membrane electrode device of the invention, the electrode prepared in thick film technique, e.g., a silver electrode, is built up in a stepped configuration by application of the paste in several layers one after another, a subsequent layer having a reduced area relative to a previously applied layer. Hereby, a dome-shaped electrode configuration is obtained which facilitates a uniform stretching of the membrane and provides suitable reservoirs for the electrolyte solution. When the electrode is a silver/silver chloride electrode, the stepped configuration offers the additional advantage that some silver chloride remains at the vertical flanks when the electrode is polished at intervals, such as is required.

The present invention will now be further described by reference to the drawings, in which

Figure 1 shows a first embodiment of an electrochemical measuring electrode device for transcutaneous measurement of the partial pressure of oxygen, viewed from the electrode side,

Figure 2 partly in sectional view the electrode housing shown in Fig. 1, viewed from a side opposite to the electrode side,

Figure 3a-3c a substrate for the first embodiment of the measuring electrode device according to the invention as shown in Figs. 1 and 2 at different stages of the production process, viewed from the same side as in Fig. 2,

Figure 4 an electrochemical measuring electrode device, slightly modified compared to the first embodiment of the measuring electrode device according to the invention shown in Figs. 1 and 2 and for transcutaneous measurement of the partial pressure of oxygen, viewed from the electrode side,

Figure 5 corresponding to Fig. 4, a second embodiment of an electrochemical measuring electrode device for transcutaneous measurement of the partial pressure of oxygen,

Figure 6 partly in sectional view a first embodiment of a combined electrochemical measuring electrode device according to the invention for combined transcutaneous measurement of the partial pressures of oxygen and carbon dioxide, viewed from the same side as in Fig. 2,

Figure 7 a detail of the combined measuring electrode device shown in Fig. 6,

Figure 8 partly in sectional view a second embodiment of a combined electrochemical measuring electrode device, viewed from the electrode side,

Figure 9 the combined electrode device shown in Fig. 8, viewed from the same side as in Fig. 2,

Figure 10 corresponding to Fig. 8, a combined electrochemical measuring electrode device including a compensation electrode,

Figure 11 the electrochemical measuring electrode device shown in Fig. 10 and includ-

ing a compensation electrode, viewed from the same side as in Fig. 2.

Figure 12 partly in sectional view an electrochemical measuring electrode device for measurement of the partial pressure of oxygen, viewed from the electrode side,

Figure 13 the electrochemical measuring electrode device shown in Fig. 12, viewed from a side opposite to the electrode side,

Figure 14 and I-E polarogram for the electrochemical measuring electrode device according to the invention shown in Figs. 1 and 2,

Figure 15 an I-t diagram for comparison of a conventional electrochemical measuring electrode device and the electrochemical measuring electrode device according to the invention shown in Figs. 1 and 2,

Figure 16 corresponding to Fig. 15, an I-t diagram for comparison of said measuring electrode devices through a longer period of time, and

Figure 17 corresponding to Fig. 15, an I-t diagram for comparison of said measuring electrode devices when measuring in vivo.

In Figs. 1 and 2, an electrochemical measuring electrode device according to the invention for transcutaneous measurement of the partial pressure of oxygen is shown. The measuring electrode device designated 1 in its entity is mounted in an electrode housing made of plastic and designated 2. The housing 2 comprises two annular components 3 and 4, the component 3 being of a larger diameter than the component 4. Two thread protrusions 5 and 6 are provided on the annular component 4 and adapted to cooperate with a corresponding thread for fastening the measuring electrode device when in use. Furthermore, a groove 7 for mounting an O-ring for fastening of an oxygen permeable membrane (not shown) is provided in the electrode housing. The measuring electrode device 1 is mounted in a recess 8 in the electrode housing 2, and a cover 9 is mounted in the electrode housing opposite to the measuring electrode device 1. Further, the interior of the electrode housing is filled with an appropriate casting 10 of, for example, epoxy. A stub 11 is provided on the exterior of the annular component 3 of the electrode housing 2 and is adapted for installation of a multicore cable 12 for connection of the measuring electrode device to external measuring apparatus (not shown).

The measuring electrode device 1 to be described in greater detail below includes a substantially plane, circular substrate 13 of a ceramic material such as beryllium oxide or aluminium oxide. As shown in Figs. 1 and 2, the substrate 13 is mounted in the housing 2 so that one of the plane sides of the substrate faces the exterior. This plane side of the substrate is designated the electrode side. On the electrode side of the substrate, a silver

anode 14 and a cathode 15 are provided, both to be described in greater detail below.

As shown in Fig. 1, the construction of the anode 14 and the cathode 15 provides several recesses 16 and 17 on the electrode side of the substrate. After mounting of the oxygen permeable membrane mentioned above, but not shown, said recesses provide reservoirs for an electrolyte. The cathode 15 mounted in a central hole in the substrate 13 comprises a glass tube 18 surrounding a platinum wire 19. As shown in Fig. 2, the platinum wire 19 is in a soldered joint 20 connected to one of the cores of the cable 12.

An NTC-resistor 21, a heating resistor 22, and a glass cover 23 are mounted on the side of the substrate opposite to the electrode side. Through soldered joints 26 and 27, terminal fields 24 and 25 on the heating resistor 22 are connected to two separate cores of the cable 12.

The reference numeral 28 designates a trace resulting from trimming the NTC-resistor 21. Said trimming may, for example, be performed by sand blasting or by means of a laser.

Fig. 3a shows the substrate 13 at a first stage of the production process. As shown on the drawings, the substrate includes two holes 29 and 30, the hole 29 being adapted for mounting of the previously mentioned cathode 15, and the hole 30 being adapted for mounting of a silver or platinum rivet 31 which is pressed into the hole and afterwards ground or polished level with the surfaces of the substrate.

As shown in Fig. 3b, five terminal fields 24, 25, 32, 33, and 34 are, in the next stage of the production process, placed on one of the plane sides of the substrate 13. The terminal fields 24 and 25 have previously been mentioned in connection with Fig. 2. The terminal field 32 is placed in conductive contact with the silver or platinum rivet 31 in order to provide electrical conductive connection between the terminal field 32 and the anode 14 at the electrode side of the substrate 13.

As shown in Fig. 3c, which shows the next stage in the production process, the terminal fields 33 and 34 are adapted for connection of the previously mentioned NTC-resistor 21. Furthermore, Fig. 3c shows the heating resistor 32 mentioned above.

The silver anode shown in Fig. 1 is applied on the opposite side of the substrate, the electrode side, also by way of thick film technique. The construction of the anode 14, which is shown in greater detail in Fig. 4, is performed in several stages. In the first stage, a layer 35 is applied, thereafter a layer 36 and a layer 37, and finally, a layer 38 is applied. As shown on the drawings, the area of the layers is reduced at each stage so that the stepped anode structure shown in pro-

duced. In combination with the previously mentioned recesses 16 and 17 also shown in Fig. 4, this stepped structure provides reservoirs for the electrolyte of the measuring electrode device.

After finishing the anode 14, the cathode 15 previously mentioned is mounted in the central hole 29 of the substrate 13, shown in Figs. 3a-3c. As shown in Fig. 4, the cathode 15 is secured in the central hole of the substrate 13 by means of a glass paste 39 of a type normally used for covering and mechanically protecting thick film circuits. On heating said glass paste to a temperature of approximately 200°C in excess of the normal heating temperature of the paste, the glass paste becomes low viscous so that it penetrates into and seals the gap between the glass tube 18 surrounding the platinum wire and the wall of the hole 29. The embodiment of the measuring electrode device according to the invention shown in Fig. 4 differs from the embodiment shown in Figs. 1 and 2 in that the NTC-resistor 21 is omitted. Instead, an NTC-resistor 40 and a glass cover (not shown) for electrical insulation of the NTC-resistor 40 relative to the anode 14 are mounted on the electrode side of the substrate 13 in the embodiment of the invention shown in Fig. 4 before the construction of the anode 14 in thick film technique. In order to provide electrical junction between the NTC-resistor 40 and the terminal fields 33 and 34, two metal rivets corresponding to the rivet 31 are pressed into two holes in the substrate corresponding to the hole 30. Only one of these metal rivets 41 are shown in Fig. 4.

However, the embodiment of the measuring electrode device according to the invention shown in Fig. 4 is not as advantageous as the embodiment shown in Figs. 1 and 2. Firstly, as mentioned above, two extra through-going junctions are required in the embodiment shown in Fig. 4 in order to provide electrical conductive connection between the NTC-resistor 40 and the terminal fields 33 and 34, whereby the assembly of the electrochemical measuring electrode device shown in Fig. 4 becomes more difficult, making the embodiment shown in Fig. 4 more expensive than the embodiment shown in Figs. 1 and 2. Secondly, the installation of the NTC-resistor 40 and the electrical insulating glass cover, not shown, results in a more uneven surface on which the anode 14 is constructed, incurring a less satisfactory membrane mounting or suspension. Thirdly, problems may arise in connection with the insulation between the NTC-resistor 40 and the silver anode 14. Fourthly, accurate adjustment of the NTC-resistor 40 is rendered impossible after the layer has been applied, and, fifthly, the thermal advantage which might be expected as a result of arranging the NTC-resistor 40 adjacent to the anode 14 is not really obtained,

partly because the electrically insulating glass cover simultaneously insulates thermally, and partly because the thermal gradient through the substrate is negligible.

Fig. 5 shows a second embodiment of an electrochemical measuring electrode device according to the invention for transcutaneous measurement of the partial pressure of oxygen. In contrast to the embodiment of the invention shown in Figs. 1-3 and the slightly modified embodiment of the invention shown in Fig. 4, the measuring electrode device shown in Fig. 5, also produced in thick film technique, is constructed on a circular substrate 42 of a ceramic material having a plane side and a convex side. At its convex side, the substrate 42 is provided with a central protrusion 43. The convex side of the substrate 42 constitutes the electrode side of the measuring electrode device, i.e. the side facing the exterior after mounting of the measuring electrode device in the electrode housing 2 shown in Figs. 1 and 2. As shown, two conical holes 44 and 45 provided in the substrate 42 are tapered outwardly towards the electrode side of the measuring electrode device and are filled up with two through-going gold or platinum junctions 46 and 47, respectively, which are provided in the corresponding holes in the following manner: With its convex side facing downwards, the substrate 42 is placed on a rubber cup which is connected to a source of vacuum through an exhaust hole. Then, two drops of gold or platinum paste are placed in the holes 44 and 45 on the plane side of the substrate. By activation of the said vacuum source, the drops of gold or platinum paste are sucked through the conical holes so that they fill up the holes. After drying and heating, the through-going gold or platinum junctions 46 and 47 are ground or polished in level with the surface of the substrate.

A layer 48 constituting the anode of the measuring electrode device is applied on the convex side of the substrate 42, i.e. the electrode side of the measuring electrode device, said layer preferably being a silver layer. The silver anode layer 48 is applied to the substrate as several layers of thick film silver paste which are applied, dried, and heated one after another. Several recesses 49 and a central recess 50 are provided in the silver anode layer 48. As shown in the drawing, the previously mentioned through-going gold or platinum junction 46 provides an electrically conductive connection between the silver anode 48 and a terminal field 51 which, like the terminal field 32 shown in Fig. 3b, is adapted to be soldered to one of the cores of the multicore cable 12. Instead of gold or platinum, a silver paste may be used for the through-going junction 46. The front area of the through-going gold or platinum junction 47 constitutes a cathode of the measuring electrode device and said through-going junction

tion is also provided with a terminal field 52 at the plane side of the substrate.

In addition to the terminal fields 51 and 52, the plane side of the substrate 42 is, such as indicated in the drawing, provided with the NTC-resistor 21 shown in Fig. 3c, the heating resistor 22 also shown in Fig. 3c, and (not shown) the corresponding terminal fields 24, 25, 33, and 34.

10 In Figs. 6 and 7, a first embodiment of an electrochemical measuring electrode device for combined transcutaneous measurement of the partial pressures of oxygen and carbon dioxide is shown. Like the embodiments of the invention discussed above, the electrochemical measuring electrode device shown in Fig. 6 is constructed on a plane, circular substrate 53, preferably of alumina, Al_2O_3 . On one side of the substrate, that is, the electrode side of the measuring electrode device, a silver anode 54 is constructed in thick film technique analogously to the anode 14 shown in Figs. 1 and 4, said silver anode comprising layers 55, 56, 57, and 58 corresponding to the layers 35-38 shown in Fig. 4. In a hole in the substrate 53, a silver rivet 59 is mounted in order to provide electrically conductive connection between the silver anode 54 and a terminal field 60 in a manner completely analogous to the manner the rivet 31 shown in Fig. 4 provides electrically conductive connection between the anode 14 and the terminal field 32. Like the embodiments of the invention shown in Figs. 4 and 5, the electrochemical measuring electrode device shown in Fig. 6 for combined transcutaneous measurement of the partial pressures of carbon dioxide and oxygen is adapted to be mounted in the electrode housing 2 shown in Figs. 1 and 2.

On the opposite side of the substrate 53, an NTC-resistor 61 corresponding to the NTC-resistor 21 shown in Fig. 3 is placed together with a heating resistor 62 corresponding to the heating resistor 22 shown in Fig. 3c. Furthermore, on the same side of the substrate 53, terminal fields 63, 64, and 65 corresponding to the terminal fields 24, 25, and 34 shown in Fig. 3c are provided (a terminal field corresponding to the terminal field 33 in Fig. 3c is also provided on the said same side of the substrate in the embodiment shown in Fig. 6, however, said terminal field is not shown in the drawing).

55 In a central hole in the substrate 53, a combined cathode and pH-electrode, designated 66, is mounted and is secured in the substrate 53 in a manner completely analogous to the manner the glass tube 18 shown in Fig. 4 is secured in the substrate 13. The combined cathode and pH-electrode 66 is shown in greater detail in Fig. 7 and is constructed on a supporting tube 67. At the exterior of the tube 67, a coating 68 of an inert metal such as gold or platinum is applied

by means of thin film technique. The inert metal coating 68 constitutes the cathode in the PO_2 measuring device. On top of the metal coating 65, an electrically insulating coating 69, e.g., of quartz glass, is applied. As can be seen from Fig. 7, an exposed area 70 of said inert metal coating 68 appears between the tube 67 and the electrically insulating coating 69. As shown in Fig. 6, a recess is provided in the coating 69 into which a wire 71 is soldered onto the inert metal coating 68 to provide electrically conductive connection between the metal coating and a terminal field 72.

80 Furthermore, the combined cathode and pH electrode includes a pH-electrode constructed in a manner known *per se*. A pH-sensitive glass membrane 73 is attached to the tube 67 and, together with the tube 67 and a plug 74, defines an inner volume in which an inner liquid 75 is confined. Further, a silver wire 76 is submerged into said liquid 75.

In Figs. 8 and 9, a second embodiment of an electrochemical measuring electrode device for combined transcutaneous measurement of the partial pressures of oxygen and carbon dioxide is shown. The embodiment of the measuring electrode device according to the invention shown in Figs. 8 and 9 is constructed on a substrate 77 of a ceramic material such as beryllium oxide or, preferably, alumina. Like the substrate 42 shown in Fig. 5, the substrate 77 has a plane side shown in Fig. 9 and a conical side shown in Fig. 8 constituting the electrode side of the measuring electrode device. A central protrusion 78 is provided on the conical side of the substrate 77 as shown in Fig. 8. In a central hole in the substrate 77 and the protrusion 78 a through-going junction 79 of an inert metal, preferably gold or platinum, is provided in a manner completely analogous to the manner the through-going gold or platinum junctions 46 and 47 are mounted in the holes 44 and 45 in the substrate 42 shown in Fig. 5. The through-going noble metal junction 79 constitutes the cathode of the measuring electrode device for PO_2 measurement. A terminal field 80 is provided on the plane side of the substrate 77 in electrically conductive connection with the through-going noble metal junction or cathode 79.

Furthermore, a layer 81, preferably a silver layer constituting both the anode for the PO_2 measurement and the reference electrode for the pH or P_{CO_2} measurement and provided by means of thick film technique, is provided on the conical side of the substrate, i.e. the electrode side of the measuring electrode device. Like the silver anode layer 48 shown in Fig. 5, the silver layer 81 is applied as several silver paste layers which are applied, dried and heated one after another. On the same side of the substrate, a silver or gold coating 82 covered by a pH-sensitive glass membrane

83 is applied. The coating 82 constitutes the pH-electrode in the combined measuring electrode device. In a manner completely analogous to the manner the through-going gold or platinum connection 46 shown in Fig. 5 provides electrically conductive connection between the anode layer 48 and the terminal field 51, through-going junctions 84 and 85 are provided in the substrate 77 for establishing electrically conductive connection between the silver electrode 81 and a corresponding terminal field 86, and between the silver or gold coating 82 and the corresponding terminal field 87, respectively.

Two reservoirs 88 and 89 for the electrolyte of the measuring electrode device are provided between the central protrusion 78 and the silver anode layer 81 and between the silver anode layer 81 and the pH-sensitive glass membrane 83, respectively.

Furthermore, on the plane side of the substrate 77, an NTC-resistor 90 corresponding to the NTC-resistor 21 shown in Fig. 3c, a heating resistor 91 corresponding to the heating resistor 22 shown in Fig. 3c, and terminal fields 92, 93, and 94 associated with said resistors are applied. As shown in Fig. 9, only three terminal fields 92, 93, and 94 are provided in contrast to Fig. 3c as the terminal field 92 is common to the NTC-resistor 90 and the heating resistor 91.

It should be noted that in the embodiments of the present invention shown in Figs. 1-4 and in Figs. 5 and 6, respectively, a terminal field common to the NTC resistor 21 and 61, respectively, and the heating resistor 22 and 62, respectively, may be provided like in the embodiment shown in Figs. 8 and 9 where a terminal field 92 common to the NTC-resistor 90 and the heating resistor 91 is provided, which has the advantage that the number of cores in the multicore cable 12 is reduced by 1.

In Figs. 10 and 11, a third embodiment of an electrochemical measuring electrode device for combined transcutaneous measurement of the partial pressures of oxygen and carbon dioxide is shown. In contrast to the embodiment shown in Figs. 8 and 9, the combined measuring electrode device according to the invention shown in Figs. 10 and 11 is constructed on a plane, circular substrate 95. The combined electrochemical measuring electrode device shown in Figs. 10 and 11 comprises a cathode mounted in a central hole in a substrate 95 and designated 96. The cathode 96 is constructed and mounted in a manner completely analogous to the manner the cathode 15 is constructed and mounted in the substrate 13 shown in Fig. 4. Thus, the cathode 96 comprises a platinum wire 98 embedded in a glass tube 97 and cast in the central hole in the substrate 95 by means of a glass paste as described above in connection with Fig. 4.

On the electrode side of the measuring electrode device, a first annular silver layer 99 is applied in thick film technique, and on top of said layer, a second annular silver layer 100 is applied. Like the silver layer 81 in the embodiment shown in Figs. 8 and 9, the annular layers 99 and 100 constitute both the anode for the Po_2 measurement and the reference electrode for pH or Pco_2 measurement.

A silver or gold layer 101 corresponding to the silver or gold layer 82 shown in Fig. 8, a pH-sensitive glass membrane 102 arranged on top of said silver or gold layer and corresponding to the pH-sensitive glass membrane 83 shown in Fig. 8, and a compensation electrode 103, made, e.g., from platinum paste or aluminum paste, are applied on the electrode side of the measuring electrode device and arranged concentrically relative to both the cathode 96 and the silver layers 99 and 100. The said compensation electrode is adapted to consume OH^- ions which are generated at the cathode 79 by reduction of O_2 and which influence the measurement of the partial pressure of carbon dioxide. The compensation electrode 103 is adapted to cooperate with associated electronic circuits forcing the current generated at the cathode by reduction of oxygen through the compensation electrode instead of through the anode.

Like in the embodiment shown in Fig. 8, reservoirs 104, 105, and 106 for the electrolyte of the measuring electrode device are arranged between the cathode 96 and the silver layers 99 and 100, between the silver layers and the pH-sensitive glass membrane 102, and between said glass membrane and the compensation electrode 103, respectively.

In order to provide electrically conductive connection between the silver anode layer 99, the silver or gold layer 101, and the compensation electrode 103 and corresponding terminal fields 107, 108, 109, respectively, silver rivets 110, 111, and 112, respectively, are fitted into holes in the substrate 95. Furthermore, an NTC-resistor 113, a heating resistor 114, and corresponding terminal fields 115, 116, and 117 are applied in thick film technique on the side of the substrate opposite to the electrode side of the measuring electrode device. Like in the embodiment shown in Fig. 9, the terminal field 115 corresponding to the terminal field 92 shown in Fig. 9 is common to both said resistors while the terminal fields 116 and 117 belong to the NTC-resistor 113 and the heating resistor 114, respectively.

According to an alternative embodiment, the stepped electrode 99, 100 is the compensation electrode made, e.g., from platinum or aluminum paste, and the electrode 103 is the silver electrode functioning both as the anode for the Po_2 measurement as the reference electrode for the pH or Pco_2 measurement.

Like the embodiments shown in Figs. 4-7, the embodiments of the electrochemical mea-

5 suring electrode device according to the invention shown in Figs. 8 and 9 and in Figs. 10 and 11, respectively, are adapted to be mounted in the electrode housing shown in Figs. 1 and 2. The mounting of the electrode devices in the electrode housing 2 may advantageously be carried out after soldering the individual cores of the multicore cable 12 onto respective terminal fields, the electrode housing 2 being heated to a temperature of approximately 80°C, and the circular substrate then being placed in the recess 8 in the electrode housing 2 shown in Fig. 2. After cooling to ambient or operation temperature, the electrode housing 2 fixes and maintains the circular substrate in place.

10 In Fig. 12 and 13, an embodiment of an electrochemical measuring electrode device for measurement of the partial pressure of oxygen is shown. In contrast to the embodiments shown in Figs. 1–11, the embodiment shown in Figs. 12 and 13 is not adapted to be mounted in any electrode housing, but constructed so that a tubular or catheter shaped device for introduction below eyelets, the tongue, the corium, or through rectum is provided. Thus, the embodiment shown in Figs. 12 and 13 is constructed on a plane substrate 118 of a ceramic material such as beryllium oxide or alumina. A silver layer 119 shaped like a J and constituting the anode of the measuring electrode device is applied onto one plane side of the substrate designated the electrode side. Like the silver anodes previously described, the silver anode 119 is produced by applying and heating several individual silver paste layers. Within the J-shaped silver anode 119, a narrow gold or platinum layer 120 constituting the cathode in the electrochemical measuring electrode device is applied onto the substrate in thick or thin film technique. Through soldered joints 121 and 122, respectively, the anode 119 and the cathode 112 are connected to two cores of a multicore cable 123. Furthermore, an insulating layer 124 covering part of the anode 119 and, such as shown in Fig. 12, covering the major part of the rod-shaped gold or platinum cathode 120 so that the exposed part of the cathode becomes approximately dot-shaped, is applied on the electrode side of the substrate 118. A membrane consisting of 1 drop 5% polystyrene solution in carbon tetrachloride and evaporated at 50–60°C is applied onto the electrodes.

55 An NTC-resistor 125, a heating resistor 126, and, on top thereof, a glass cover 127, are applied onto the other plane side of the substrate 118 in thick film technique. Like in the previously described embodiments of the present invention, the NTC-resistor 125 and the heating resistor 126 are mounted in electrically conductive connection with associated terminal fields 128, 129, and 130, 131, respectively. Through soldered joints 132,

133, and 134, 135, respectively, the terminal fields are connected to cores in the multicore cable 123.

70 After soldering the individual cores of the multicore cable 123 onto corresponding terminal fields 128–131 and onto the anode 119 and the cathode 120, the substrate 118 is cast into a casting 136 of, e.g., epoxy. The casting 136 fills the interior of the multicore cable 123 and fixes the substrate 118 of the electrochemical measuring electrode device relative to an outer insulating jacket 137 of the multicore cable 123. In Figs. 12 and 13, the outer insulating jacket 137 of the multicore cable 123 is shown in dotted line reaching beyond the soldered joints through which the multicore cable is connected to respective terminal areas and to the anode and the cathode.

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Example 1.

In a preferred embodiment of the device shown in Figs. 1 and 2, the substrate was an alumina substrate of the type Kyocera A476 which has a diameter of 10.5 mm and a thickness of 0.63 mm, and which is provided with two 1 mm holes, one at the centre and one offset 3.5 mm. The silver rivet was a sterling silver wire with a diameter of 1 mm and was fitted into the center hole and exposed to mechanical pressure from both sides. A silver paste of the type ESL 9990 (ESL: Electroscience Laboratories, Pennsylvania, USA) was used for the anode, an NTC-resistor paste of the type emca 5013-ITM (emca: Electronic Materials Corporation of America, New York, USA) was used for the NTC-resistor, and a heating resistor paste of the type emca 5011-1 was used for the heating resistor. A silver/Pd paste of the type emca 6095S was used for the terminal fields, and a glass cover paste of the type emca 2274 was used for the glass cover.

The cathode consisted of a Pt wire with a diameter of 24 μm and embedded in a glass tube of soda-lime glass having a diameter of 1 mm and being of the type jena N16 and was cast into the substrate by means of a glass cover paste of the type emca sealing glass 2079. According to the specification from the manufacturer, the glass cover paste should be fired at a temperature between 450°C and 550°C for a period of 10 minutes. However, in order to obtain low viscous properties, the glass cover paste was fired at a temperature of 690°C for a period of 10 minutes.

120 After the firing, the NTC-resistor layer had a thickness of 20–25 μm , the heating resistor layer had a thickness of 16 μm , the terminal areas had a thickness of 12 μm , and the glass cover had a thickness of 12–16 μm .

The substrate was pressed into an electrode housing of the type Radiometer at a temperature of 80°C. The interior of the electrode housing was filled up with epoxy of the type

Scotchcast No. 250 and was hardened for two days at a temperature of 65°C. The cover of the electrode housing was of the type Radiometer. The silver anode had an average thickness of 65 μm so that a minimum life time of two years with a maximum current of 50 nA was guaranteed within a security factor of 10. The silver anode was constructed as four approximately 30 μm thick layers which were applied, dried, and heated individually. The electrolyte solution used for this electrode device consisted of 0.1 M KCl, 0.05 M NaHCO_3 , and thymol in propylene glycol. 15 μm thick polypropylene was used as the membrane.

Example 2.

The same electrode device as in Example 1 was made, but a pure silver wire was used for the rivet instead of the sterling silver wire.

Example 3.

The same electrode device as in Example 1 was made, but instead of a silver paste of the type ESL9990, a silver paste of the type emca 7069 was used; a glass cover paste of the type emca glass 101 was used for casting the cathode into the substrate, and a lead glass tube was used for embedding the platinum wire instead of a glass tube of soda-lime glass. Instead of an NTC-resistor paste of the type emca 5013-ITM, and NTC-resistor paste of the type ESL2413 was used, and instead of a heating resistor paste of the type emca 5011-1, a heating resistor paste of the type ESL3911 was used. Instead of a membrane of polypropylene, a 25 μm polytetrafluoroethylene membrane was used.

Example 4.

In a device of the kind shown in Fig. 5 or 8, a gold paste of the type emca 6360 or a platinum paste of the type ESL5542 was used as cathode paste. Instead of a gold paste of the type emca 6360, a gold paste of the type emca 3264 could be used for the cathode paste.

In Fig. 14, an I-E polarogram for the electrochemical measuring electrode device for measurement of the partial pressure of oxygen shown in Figs. 1 and 2 is shown. In Fig. 14, the electrode current is indicated as a function of the anode cathode voltage, the measurement being performed in ambient atmosphere. The curve was recorded by means of a recorder, the anode-cathode voltage being varied continuously for 1 minute and thereafter being maintained at a fixed value for 1 minute in order to allow the electrochemical measuring electrode device to reach steady state. The curve 1 shows the curve recorded for a voltage increased from 0 to 1.3 V, and the curve 2 shows the curve recorded for a voltage decreased from 1.3 to 0 V. It will be noted that the curves show a desirably

broad plateau of the voltage sensitivity of the electrode device and that said plateau is ideally located around the anode-cathode voltage of 630 mV which is conventionally used, and that the curves for increasing and decreasing voltage, respectively, are almost coinciding so that the electrode device is free of hysteresis. The curve 3 is a curve indicating the zero current of the measuring electrode device, said zero current being completely negligible (less than 1 mm Hg), such as shown in Fig. 14.

In Fig. 15, two curves are shown, one in dotted line, designated C, for a conventional transcutaneous polarographic oxygen measuring electrode device (Radiometer type E 5240) and one, in full line and designated N, for a transcutaneous polarographic oxygen measuring electrode device according to the present invention. The curves indicate the electrode current I as function of time t recorded partly in ambience (A) and partly with a drop of sulphite placed on the membrane of the measuring electrode device (S), the anode-cathode voltage applied being 630 mV. The curves N and C shown in Fig. 15 were recorded with the corresponding measuring electrode devices thermostatically controlled at a temperature of 43°C. The displacement of the curves along the t -axis is caused by a completely physical displacement of the corresponding pens of the recorder (pen offset). As seen from the drawing, the measuring electrode device according to the invention has the same short response time as the conventional measuring electrode device and approximately the same sensitivity (approximately 12 pA/mm Hg) as the conventional measuring electrode device.

In Fig. 16, two curves corresponding to the curves shown in Fig. 15 were recorded for the same measuring electrode devices as in Fig. 15, but for a significantly longer period of time, 62 hours. The figure indicates that the long time drift of the two measuring electrode devices are practically identical. Thus, the electrode current of the measuring electrode device according to the invention drifts less than corresponding to 4 mm Hg.

In Fig. 17, two curves corresponding to the curves shown in Fig. 15 are shown indicating in vivo measurements using the conventional measuring electrode device (C) and using the measuring electrode device according to the invention (N). Like in Figs. 15 and 16, the curves shown in Fig. 17 are approximately identical. The difference between the curves, apart from the displacement between the respective pens, is primarily caused by the physical placing of the measuring electrode devices on the test subject. Thus, at D, both measuring electrode devices show a decrease in electrode current caused by the test object holding his breath. Furthermore, at E, F, and G, both measuring electrode devices show

decreases in the electrode current caused by blocking the blood circulation. At H, the curve C shows a minor bulge caused by supply of external pressure to the measuring electrode device.

CLAIMS

1. An electrochemical measuring electrode device comprising an electrically insulating substrate and at least one electrode prepared in thick film technique and arranged on one side of the substrate, the device comprising electrically conductive means adapted for establishment of electrical connection to the electrode and provided on a side of the substrate which is different from the side on which the electrode is arranged,

characterized in that the electrical junction between the electrode prepared in thick film technique and said electrically conductive means is constituted by an electrical conductor arranged in a through-going passage in the substrate.

2. An electrochemical measuring electrode device according to claim 1,

characterized in that the substrate has a plane or plane-convex shape, and that said electrically conductive means are provided on the plane side of the substrate.

3. An electrochemical measuring electrode device according to claim 1 or 2,

characterized in that said electrically conductive means are constituted by a connection or terminal field.

4. An electrochemical measuring electrode device according to claim 3,

characterized in that the connection or terminal field is prepared in thick film technique.

5. An electrochemical measuring electrode device according to any of the preceding claims,

characterized in that the electrical conductor arranged in a through-going passage in the substrate is a metal rivet press-fitted into the passage.

6. An electrochemical measuring electrode device according to any of claims 1-4,

characterized in that the electrical conductor arranged in a through-going passage in the substrate is constituted by a body of metal paste or metal solidified in the passage.

7. An electrochemical measuring electrode device according to any of the preceding claims,

characterized in that it further comprises a thermostating circuit applied on the substrate in thick film technique.

8. An electrochemical measuring electrode device according to claim 7, characterized in that the thermostating circuit is arranged on a side of the substrate which is different from the side on which the electrode prepared in thick film technique is arranged.

9. An electrochemical measuring electrode device according to any of the preceding

claims,

characterized in that the electrode prepared in thick film technique is a silver electrode.

10. An electrochemical measuring electrode device according to claim 9 for the measurement of the partial pressure of oxygen and having a cathode of a noble metal and an anode,

characterized in that the silver electrode prepared in thick film technique constitutes the anode of the measuring electrode device.

11. An electrochemical measuring electrode device according to claim 10,

characterized in that the cathode is constructed as a noble metal wire, preferably a platinum wire, which extends through the substrate in an electrically insulating encasing.

12. An electrochemical measuring electrode device according to claim 10 or 11,

characterized in that the cathode is constructed as a noble metal wire embedded in a glass tube and cast in a hole in the substrate by means of a glass paste.

13. An electrochemical measuring electrode device according to claim 10,

characterized in that the cathode is constituted by a body of noble metal paste or noble metal solidified in a through-going passage of a diameter of about 1-100 μm , e.g., 10-100 μm in the substrate, the front area of said body constituting the active measuring surface of the said cathode.

14. An electrochemical measuring electrode device according to claim 13,

characterized in that the said body consists of platinum or of solidified gold or platinum paste.

15. An electrochemical measuring electrode device according to any of the preceding claims,

characterized in that the through-going passage or passages in the substrate is/are provided by means of a laser.

16. An electrochemical measuring electrode device according to claim 9 for the measurement of the partial pressure of carbon dioxide and having a pH-sensitive electrode and a reference electrode,

characterized in that the silver electrode prepared in thick film technique constitutes the reference electrode of the measuring electrode device.

17. An electrochemical measuring electrode device according to claim 9 for the simultaneous measurement of the partial pressures of oxygen and carbon dioxide and having a cathode of a noble metal and an anode for the oxygen measurement, and a pH-sensitive electrode and a reference electrode for the carbon dioxide measurement,

characterized in that the silver electrode prepared in thick film technique constitutes the reference electrode.

18. An electrochemical measuring electrode device according to claim 9 for the

simultaneous measurement of the partial pressures of oxygen and carbon dioxide and having a cathode of a noble metal and an anode for the oxygen measurement, and a pH-sensitive electrode and a reference electrode for the carbon dioxide measurement,

characterized in that the silver electrode prepared in thick film technique constitutes the anode.

19. An electrochemical measuring electrode device according to any of the preceding claims and for measurement of the partial pressure of one or several gases in a liquid or in a gas mixture, characterized in that the electrode prepared in thick film technique, together with a membrane permeable to the gas or gases the partial pressure or pressures of which is/are to be measured, defines a reservoir for an electrolyte solution, and that the electrode prepared in thick film technique has a stepped configuration.

20. A method for preparing an electrochemical measuring electrode device in which an electrode is applied in thick film technique on an electrically insulating substrate,

characterized by the steps of introducing a metallic conductor into a through-going passage in the substrate, and applying, in thick film technique, an electrode layer on the substrate in electrically conductive connection with said metallic conductor.

21. A method according to claim 20, characterized by further applying a connection or terminal field in thick film technique in electrically conductive connection with the metallic conductor and on a side of the substrate which is different from the side on which the electrode layer is applied.

22. A method according to claim 20 or 21,

characterized by the further introductory step of establishing the through-going passage by means of a laser.

23. A method according to any of claims 20-22,

characterized in that the introduction of the metallic conductor is performed by press-fitting a metal rivet into the passage.

24. A method according to any of claims 20-22,

characterized in that the introduction of the metallic conductor is performed by solidifying a molten metal or a metal paste in the passage.

25. A method according to claim 24 characterized by introducing the molten metal or the metal paste into the passage by applying a pressure difference between opposite sides of the substrate.

26. A method according to any of claims 20-25,

characterized by applying the electrode in several layers on top of each other.

27. A method according to claim 26, characterized by applying, on top of a previ-

ously applied electrode layer, an electrode layer having a reduced area relative to said previously applied electrode layer to provide a stepped configuration of the final electrode.

28. A method for preparing an electrochemical measuring electrode device or a component therefor,

characterized by providing a metallic conductor in a through-going passage in an electrically insulating substrate by solidifying a molten metal or a metal paste in the through-going passage.

29. A method according to claim 28, characterized by providing an electrode of the electrode device by solidifying a electrode metal or electrode metal paste in the through-going passage.

30. A method according to any of claims 20-29 for the preparation of a measuring electrode device, or a component therefor, comprising a noble metal cathode,

characterized by solidifying a molten noble metal or a noble metal paste in a through-going passage in the electrically insulating substrate.

31. A method according to any of claims 20-29 for the preparation of a measuring electrode device, or a component therefor,

characterized by casting an electrode, embedded in a glass tube, into a through-going passage in the electrically insulating substrate by introducing a glass paste into the gap between said glass tube and the wall of said passage by heating said glass paste to such a temperature in excess of the normal heating temperature of the glass paste that it becomes low viscous and stops and seals said gap, and allowing the glass paste to solidify by cooling.

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